Properties of Ceramic Candle Filters

Jack D. Spain (spain@sri.org)
H. Stuart Starrett (starrett@sri.org)
Southern Research Institute
757 Tom Martin Drive
Birmingham, Alabama 35211

Introduction

Coal-fired Pressurized Fluidized Bed Combustion (PFBC) and Integrated Gasification Combined Cycle (IGCC) systems require ceramic candle filter elements which can withstand the mechanical, thermal, and chemical environment of hot gas cleanup applications. These systems demand filter elements to sustain the thermal stresses of normal operations (pulse cleaning), of start-up and shut-down conditions, and of unanticipated process upsets such as excessive ash accumulation without catastrophic failure. The filter elements must also survive the mechanical loads associated with handling and assembly, normal operation, and process upsets.

Schumacher F40 and Pall 442T clay-bonded SiC particle candle filters and Coors P-100A-1 alumina mullite candle filters tested in PFBC applications resulted in failure of some candles. The Coors monolithic ceramic was susceptible to thermal stresses while the clay-bonded SiC particle materials showed substantial creep and degradation of the binder. Schumacher and Pall manufactured SiC particle candle filters with a different binder - Schumacher FT20 and Pall 326 - intended to decrease the creep rate. Test results on as-manufactured Schumacher FT20 and Pall 326 indicate that the creep rate has indeed been decreased by about an order of magnitude and the temperature where creep begins to occur has been increased by 100 °F to 200 °F; however, creep continues to be seen in testing at 1600 °F and above and was observed at 1562 °F in-service at Karhula. The creep resistance comes at the price of reduced room temperature strength, although the FT20 and 326 materials have nearly the same strength as the F40 and 442T materials in the operating temperature range. Axial tensile, hoop tensile, tensile creep, thermal expansion, and thermal conductivity properties were measured on these materials as-manufactured, after 540 hr. of PFBC service, and after 1166 hr. of PFBC service. Tests performed after PFBC service have provided an indication of these material's ability to survive long-term in the hot gas cleanup environment. Testing of FT20 and 326 materials after 540 hrs. and 1166 hrs. in PFBC service showed that property degradation occurred but less than was seen in F40 and 442T materials. The stress-strain curves for FT20 and 442T at room temperature became nonlinear after service in the PFBC possibly due to additional porosity and matrix cracks. Microstructural examinations of Schumacher F40 and Pall 326 have been used to provide material models which explain

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the behavior of these materials. These material models have shown that the behavior of the candle filters is controlled by the ceramic binder. Evidence indicates that the binder in both of these materials is a non-translucent clay with alumina and some free glass (free silica) and that characteristics of glass such as chemical attack in the presence of acid, high temperature creep, and stress rupture will be seen in Schumacher FT20 and Pall 326. Considerable observations indicate that the matrices are still glass limited.

Objectives

Objectives of the test program at Southern Research are as follows:

1. Provide material characterization to develop an understanding of the physical, mechanical, and thermal behavior of hot gas filter materials.

2. Develop a material property data base from which the behavior of materials in the hot gas cleanup environment may be predicted.

3. Perform testing and analysis of filter elements after exposure to actual operating conditions to determine the effects of the thermal and chemical environments in hot gas filtration on material properties.

4. Explore the glass-like nature of the matrix material.

Approach

Based on the anticipated operating conditions in the hot gas cleanup environment and on the in-service performance of candle filters tested to date, several critical issues have been identified for candle filter materials. The filter materials must possess sufficient mechanical strength to withstand the loads generated during handling and assembly, normal operation, and process upsets. Candle filters must sustain the thermal stresses generated during pulse cleaning, start-up and shut-down, and process upsets. Creep is a key issue because excessive creep led to failure of some Schumacher F40 and Pall 442T filters. Filter materials must operate in the PFBC and IGCC environments without excessive property degradation. Finally, the materials must filter effectively with acceptable pressure drops. Southern's approach is to measure basic material properties of the candle filter materials and predict in-service performance based on the material properties. The properties measured address the critical issues discussed above. For example, mechanical strength is addressed by tensile and compressive strength measurements while thermal stress susceptibility is addressed by measuring tensile stress-strain responses and thermal expansion. A summary of critical issues and Southern's methods for evaluation of each issue is given in Table 1.

Test results presented in this paper are for Schumacher FT20 and Pall 326 materials. These materials were evaluated in as-manufactured condition according to the test matrix given in Table 2 and after 540 hrs. at 1560 °F and after 1166 hrs. at 1560 °F in service at Karhula according to the test matrix given in Table 3.

Table 1
Critical Material Issues and Methods of Evaluation

Material Issue	Methods for Evaluation
Mechanical Strength, “Toughness”	Tensile Strength Compressive Strength Fracture Toughness
Thermal Stress Susceptibility	Tensile Stress-Strain Curve Thermal Expansion
Creep	Tensile Creep/Heat Deflection
Property Degradation	Tensile Stress-Strain After Exposure Ring Tensile After Exposure Microstructure
Filtration/Pressure Drop	Permeability
Glass-like nature of matrix	Microscopy, SEM, x-ray diffraction, EDS

Table 2
Test Matrix for Pall 326 and Schumacher FT20 Candle Filter Materials

		Test Temperature			
Test Type	**Direction**	**RT**	**1600 °F**	**1700 °F**	**1800 °F**
Tensile	Hoop	9			
	Axial	4	4	4	4
Tensile Creep	Axial		4	4	
Thermal Expansion	Axial	2--->			
Thermal Cond.	Radial	2-->			
Microstructure		x			

Table 3
Test Matrix for Pall 326 and Schumacher FT20 Candle Filter Materials After 540 and 1166 Hours at 1560 °F In Service at Karhula

		Test Temperature			
Test Type	**Direction**	**RT**	**1600 °F**	**1700 °F**	**1800 °F**
Tensile	Hoop	9[1]			
	Axial	3			
Tensile Creep	Axial		4[2]	4[2]	
Thermal Cond.	Radial	2-->			
Microstructure		x			

1. Hoop tensile testing was performed only on material with 540 hrs. in service.
2. Only one creep specimen was tested after 1166 hrs. in service.

Results

Schumacher FT20

One of the key material issues for hot gas filter materials has been strength degradation with time in service. Southern has used room temperature tensile testing on candle filters removed from service to monitor retained mechanical strength. Axial tensile stress-strain responses at room temperature are shown in Figure 1 for Schumacher FT20 as-manufactured, after 540 hrs. at 1560 °F in service, and after 1166 hrs. at 1560 °F in service. The responses were linear all the way to failure for as-manufactured specimens and became bilinear after service at Karhula. The shape of the curves was about the same for the specimens with 540 hrs. in-service as for the specimens with 1166 hrs. in-service. Perhaps the change in stress-strain response was caused by matrix compliance due to lost matrix material after service in the PFBC. Some special work, including microscopic examination of fractured tensile specimens, is needed to fully explain the change in shape of the stress-strain curves.

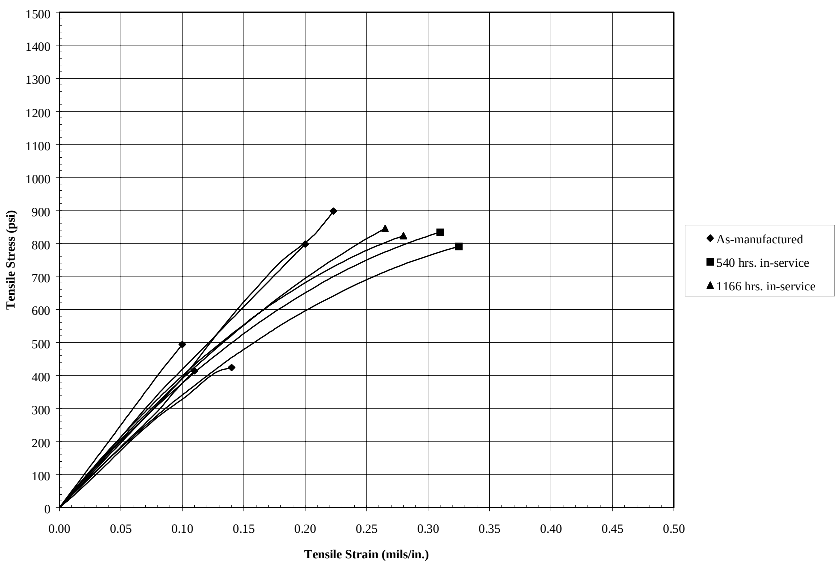

Figure 1. Tensile Stress-Strain Responses at Room Temperature for Schumacher FT20

Room temperature tensile strengths in both the axial and hoop directions are plotted versus time in service in Figure 2. The results obtained in the hoop direction indicate a decrease of ~10% in tensile strength after 540 hrs. in service. In the axial direction, a large specimen-to-specimen variability was seen in tensile strength of the as-manufactured specimens which made strength comparisons between the different conditions difficult. However, based on the higher strength as-manufactured specimens, the axial tensile strength is near the same after 540 hrs. or 1166 hrs. in service at 1560 °F as in as-manufactured condition. Taken together, the axial and hoop tensile strengths indicate that the tensile strength may decrease slightly, up to ~10%, over the first 540 hrs. and then remain the same from 540 hrs. to 1166 hrs..

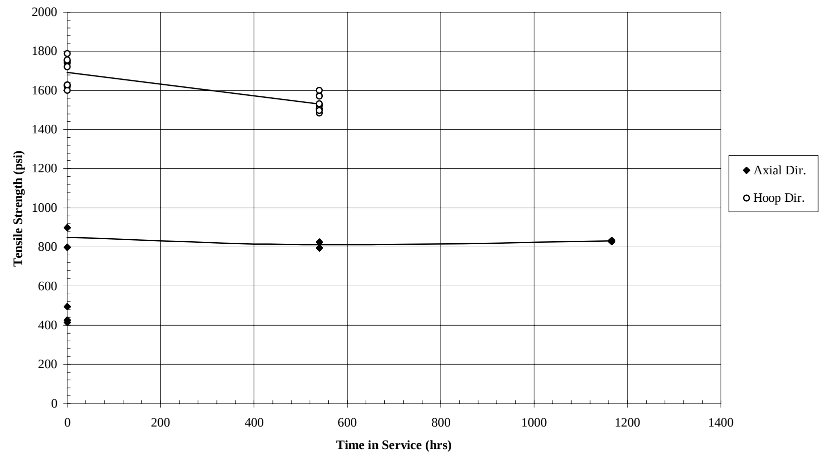

Figure 2. Ultimate Tensile Strength Versus Time in Service for Schumacher FT20

Creep strain versus time responses obtained for Schumacher FT20 are shown in Figure 3. The responses consisted of an initial region and a secondary region with the creep rate about an order of magnitude greater in the initial region. The initial creep rate at 1600 °F ranged from 3.2 x 10^{-5} in./in./hr. with a 300 psi load to 11.3 x 10^{-5} in./in./hr. with a 500 psi load. Two secondary creep rates, 1.5 x 10^{-6} in./in./hr. with a 250 psi load and 2.1 x 10^{-6} in./in./hr. with a 500 psi load, were obtained at 1600 °F. At 1700 °F, initial creep rates of 5.1 x 10^{-5} in./in./hr. with a load of 250 psi and 14.8 x 10^{-5} in./in./hr. with a load of 500 psi were obtained and one secondary creep rate of 1.0 x 10^{-5} in./in./hr. with a load of 250 psi was obtained. The specimen tested at 1700 °F, 500 psi had already been tested at 1600 °F, 500 psi for 114 hrs.. The creep response of one Schumacher F40 specimen at 1400 °F is included in Figure 3 for comparison. As shown, the creep rate of

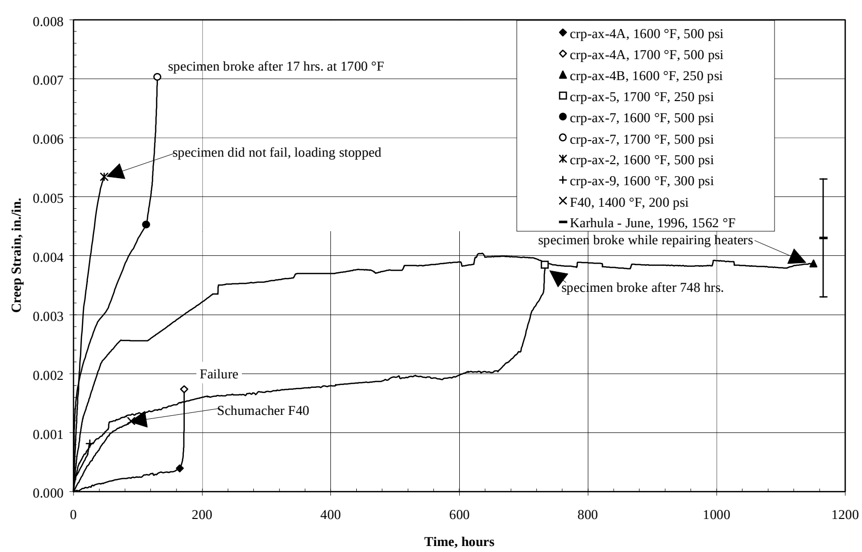

Figure 3. Creep Strain Versus Time for Schumacher FT20

F40 at 1400 °F is comparable to the creep rate of FT20 at 1600 °F. Also, note that stress rupture occurred several in several FT20 specimens.

Westinghouse reported elongation of some candle filters, including Schumacher FT20, after removal from the PCFBC at Karhula in November, 1996 following 1166 hrs.

of operation at 1560 °F. The elongations measured ranged from 5 - 8 mm (0.2 - 0.3 in.), representing creep strains of 0.0033 in./in. to 0.0052 in./in.. The range of creep strains observed after 1166 hrs. in service at Karhula is plotted in Figure 3. Direct comparison of the elongations measured after service in Karhula and the creep strains measured in tensile creep tests is difficult because the loads in Karhula are not known; however, the loads in Karhula probably were much smaller than the 250 psi or 500 psi loads used for creep tests. Agreement between the measured creep strains and the measured elongations after service in Karhula appears reasonable, certainly within an order of magnitude, although if the loads in Karhula were indeed smaller than in the creep tests, then less elongation in service at Karhula would be expected based on the measured creep rates. This indicates that the long-term exposure to the hot gas filtration environment may affect the creep behavior of the Schumacher FT20 material. Creep testing of material removed from Karhula is in progress at Southern and will provide some indication of the effect of the hot gas filtration on creep performance.

The Schumacher FT20 creep specimens were susceptible to stress rupture at 1700 °F. The duration of the 1700 °F tests before failure occurred ranged from 7 hrs. with a 500 psi load to 748 hrs. with a 250 psi load. Only one specimen failed during creep testing at 1600 °F and that specimen failed after 25 hrs. at 300 psi. The failure of creep specimens at 1700 °F and 500 psi load (or 250 psi for one specimen) might or might not be an important issue, depending on the required operating temperature and the operating loads. If these candles are to operate in the temperature range of 1600 °F to 1700 °F, then creep testing in the future must determine the maximum temperature and the maximum load level at which the FT20 material can operate without creep failure.

Unit thermal expansion of Schumacher FT20 and F40 are shown in Figure 4.

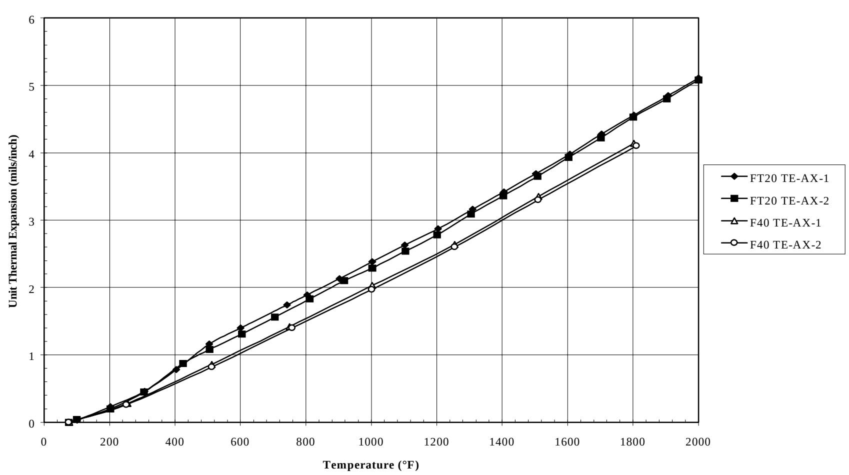

Figure 4. Unit Thermal Expansion of Schumacher FT20 and F40

A “knee” in thermal expansion curve for FT20 was seen at 300 °F to 500 °F which was not seen for F40. Other ceramics such as pyroceram, cordierite, and quartz-bearing clays show a similar behavior. Return to zero on cool-down indicates that the knee in the curve probably represents a reversible phase transformation. From 500 °F up, the shape of the thermal curves for FT20 and F40 was similar; therefore, the materials have nearly the same coefficient of thermal expansion (CTE) in the operating range.

Microstructural examinations of Schumacher FT20 and Pall 326 are still in progress but the initial findings are presented here. Photomicrographs taken at ~200X of Schumacher FT20, as-manufactured and after 1166 hrs. in-service at Karhula, are shown in Figures 5 and 6.

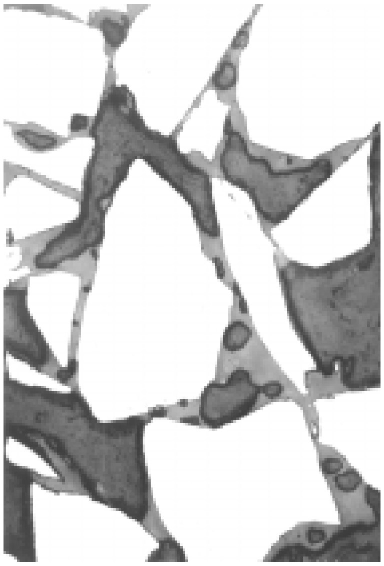

Figure 5. Photomicrograph of As-Manufactured Schumacher FT20 Taken at 200X

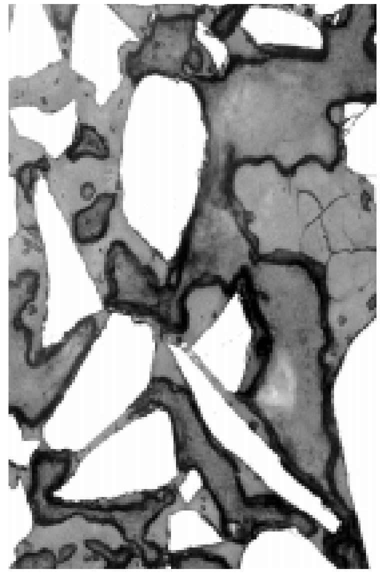

Figure 6. Photomicrograph of Schumacher FT20 After 1166 Hrs. In-Service at Karhula Taken at 200X

The photomicrographs indicate that this material consists of SiC particles connected by bridges of ceramic binder material. The binder does not typically cover the entire perimeter of the SiC particles but rather forms a bridge between adjacent particles. Small pores and cracks are seen throughout the binder material. Pores and cracks in the binder weaken the candle filters although the structure, individual particles connected by bridges of matrix, provide an inherent "toughness" since cracks cannot propagate readily. The pores seen in the binder have curved boundaries with no sharp corners. This is typical of amorphous materials like glass whereas pores formed in crystalline materials typically have straight edges and sharp corners. A cube of FT20 measuring 1/4 - 3/8 inch on each side was placed in hydrofluoric acid and within 2 hrs. at 70 °F the binder material was removed. The binder appears to be a non-translucent clay with alumina and some free glass (free silica). The photomicrograph of FT20 after 1166 hrs. in-service shows evidence of chemical attack around the edges of the binder material. Some pores in the binder after service at Karhula are open on the edges of the binder. These open edge pores and the rough surface are evidence of chemical attack around the edges of the binder. These photomicrographs show that like the properties of Schumacher F40, properties of FT20 are controlled by the properties of the binder. Alumina was found by energy dispersive spectroscopy (EDS) of the solid and by diffraction of binder residue after reaction with hydrofluoric acid. Also, there were white particles in the residue after reaction with hydrofluoric acid. The free silica in the FT20 binder means the characteristics of clay, including high temperature creep and susceptibility to chemical attack in the PFBC environment, will be seen in this material;

however, property measurements and microstructural examination both indicate that Schumacher FT20 showed improvements over Schumacher F40.

Future testing of Schumacher FT20 will focus on determining operating limits including maximum temperature, load level, and time in-service. Tensile evaluations will be used to assess property degradation in the PFBC environment, creep tests on as-manufactured and used filters will be used to assess load and temperature levels where this material can operate without creep failure, microstructural examinations including energy dispersive x-ray analysis and x-ray diffraction of residual binder material after dissolving in hydrofluoric acid will be used to better define the chemical properties of the binder, and higher magnification photomicrographs and scanning electron microscopy (SEM) will be used to examine the integrity of the particle/binder interface.

Pall 326

Axial tensile stress-strain responses at room temperature are shown in Figure 7 for Pall 326 as-manufactured, after 540 hrs. at 1560 °F in service, and after 1166 hrs. at 1560 °F in service. As seen in the Schumacher FT20 specimens, the stress-strain responses for

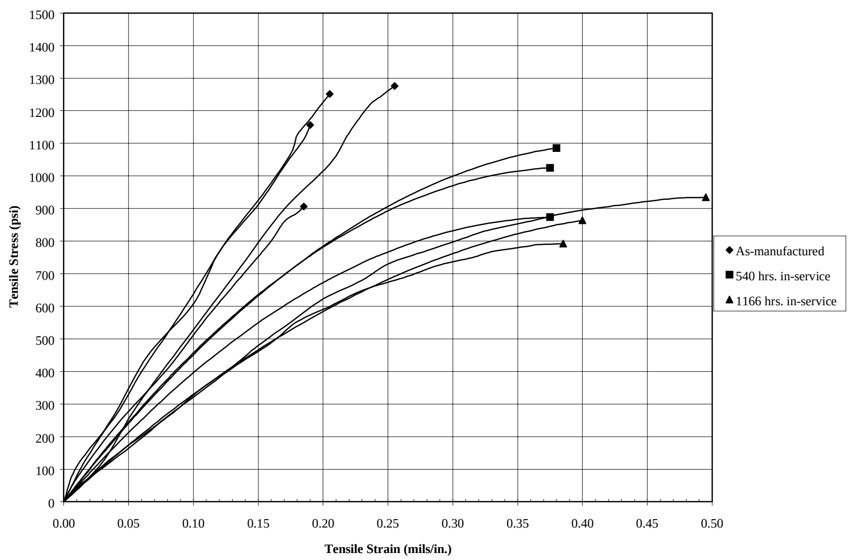

Figure 7. Tensile Stress-Strain Responses at Room Temperature for Pall 326

as-manufactured specimens were nearly linear to failure but became nonlinear after service at Karhula, perhaps caused by matrix compliance due to lost binder material and matrix cracking. The specimens tested after 1166 hrs. in-service rolled over more than the specimens tested after 540 hrs. in-service. Room temperature tensile strengths in both the axial and hoop directions are plotted versus time in service in Figure 8. In the hoop direction, the tensile strength decreased ~33%, from 2130 psi to 1430 psi, after 540 hrs. in service. In the axial direction, the tensile strength decreased ~14%, from 1150 psi to 990 psi, after 540 hrs. in service and decreased ~25%, to 860 psi, after 1166 hrs. in service. Considerable specimen-to-specimen variability was seen in tensile strength. One as-manufactured specimen had an axial strength of 1990 psi, ~73% more than the other specimens. This strength value is not included in the average value of 110 psi

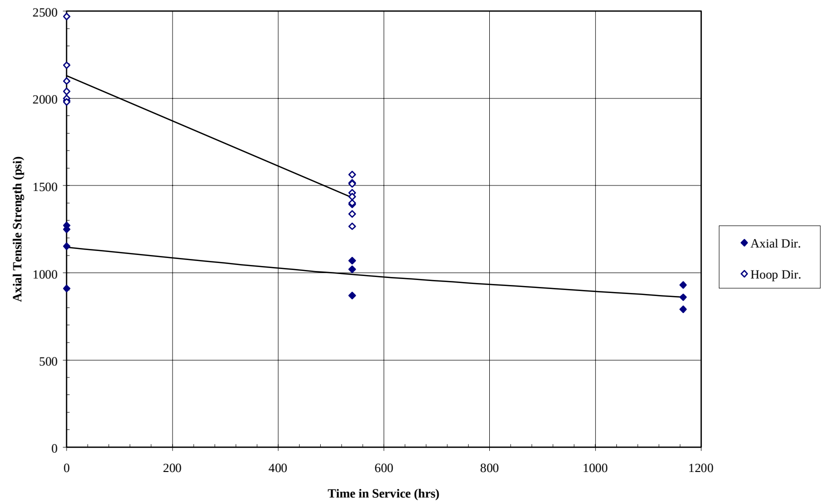

Figure 8. Ultimate Tensile Strength Versus Time in Service for Pall 326

discussed above. In comparison with Schumacher FT20, the strength of Pall 326 degrades more with time in the hot gas filtration environment. After 1166 hrs., the strength of Schumacher FT20 appears to have leveled off (quit decreasing) whereas the strength of Pall 326 may decrease further with additional time in service. Because Pall 326 has a higher as-manufactured tensile strength than Schumacher FT20, the two materials have nearly the same axial strength after 1166 hrs. in service even though the strength degradation was greater for Pall 326.

Creep strain versus time responses obtained for Pall 326 are shown in Figure 9. The responses were similar for Schumacher FT20 and Pall 326; that is, the responses consisted of an initial region and a secondary region with the creep rate about an order of magnitude greater in the initial region. Two specimens were tested with tensile loads of 200 and 250 psi at temperatures of 1500 °F to 1800 °F and no creep was measured. The remaining specimens, including all of those shown in Figure 9, were tested with a tensile load of 500 psi. While there was substantial specimen-to-specimen variability, the initial creep rates at 1600 °F, 500 psi were typically 10^{-5} - 10^{-4} in./in. and the secondary creep rates at that temperature and stress level were typically an order of magnitude lower. These creep rates were similar to the values obtained for Schumacher FT20. Creep results obtained for three Pall 442T specimens are included in Figure 8 for comparison. Digitized curves were not available for these three 442T specimens so only the endpoints are plotted. As shown, the creep rate of 442T at 1550 °F, 200 psi was similar to the creep rate of 326 at 1600 °F, 500 psi. The Pall specimens were not as susceptible to breaking as the Schumacher specimens. One specimen broke at 1700 °F, 500 psi after 179 hrs. and one specimen broke (in the grip area) at 1800 °F, 500 psi after 134 hrs.. However, stress rupture was again active.

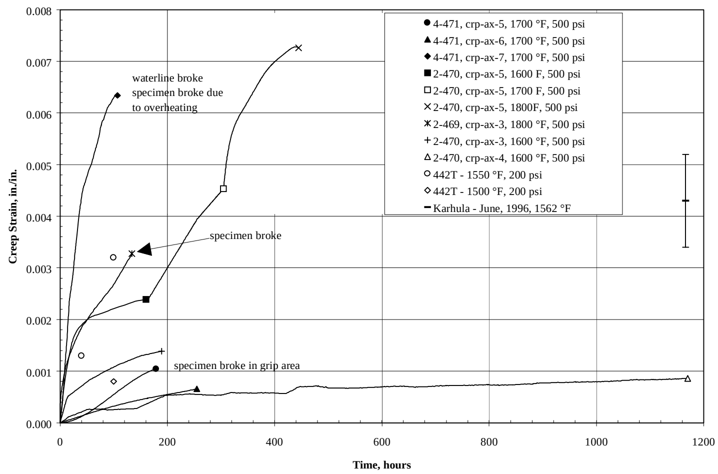

Figure 9. Creep Strain Versus Time for Pall 326

The 5 - 8 mm elongation reported by Westinghouse for candle filters removed from Karhula in November, 1996 after 1166 hrs. at 1560 °F is plotted in Figure 9. Only one Pall creep specimen has been tested this long and the total creep measured was less than was measured after service in Karhula. If the results of the 200 hr. creep tests are extrapolated to 1166 hrs. (a considerable extrapolation), the total creep would be near the values measured after removal from Karhula. Since the creep tests were conducted with a 500 psi load, and the load at Karhula, although it was unknown, was not likely that high, the elongations seen after service at Karhula appear greater than would be predicted based on creep strains measured in creep tests. This indicates that the PFBC environment affected the creep behavior. Creep testing on material removed after PFBC service at Karhula is in progress to determine the effect of this environment.

Unit thermal expansion of Pall 326 and 442T are shown in Figure 10. The “knee” in thermal expansion curve which was seen for Schumacher FT20 at 300 °F to 500 °F was seen for Pall 326 also. Return to zero on cool-down indicates that the knee in the

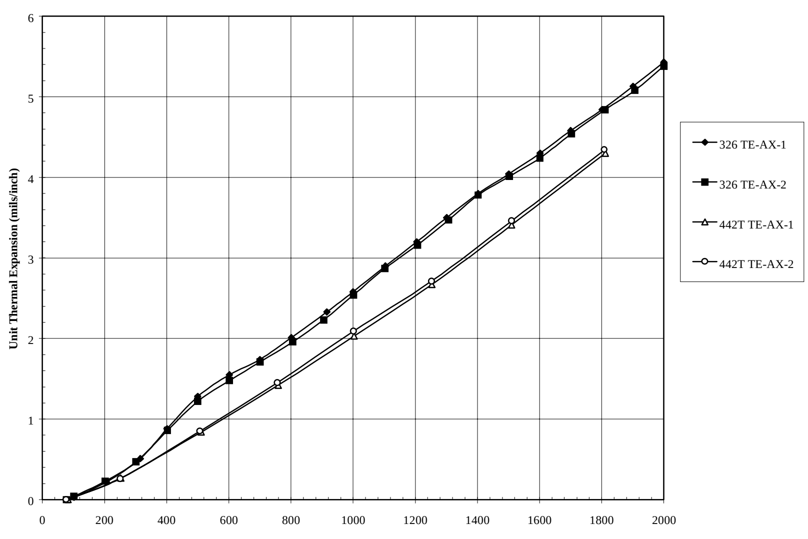

Figure 10. Unit Thermal Expansion of Refractron 326 and 442T

curve probably represents a reversible phase transformation. From 500 °F up, the shape of the thermal curves for 326 and 442T were similar; therefore, the materials have nearly the same coefficient of thermal expansion (CTE) in the operating range. A small knee in the thermal expansion curve for Pall 326 was seen at 1400 °F, possibly indicating the formation of tridymite or cristobalite in the binder material at this temperature. This was not seen in any of the other materials tested in this program.

Photomicrographs taken at ~200X of Pall 326, as-manufactured and after 1166 hrs. in-service at Karhula, are shown in Figures 11 and 12. The photomicrographs

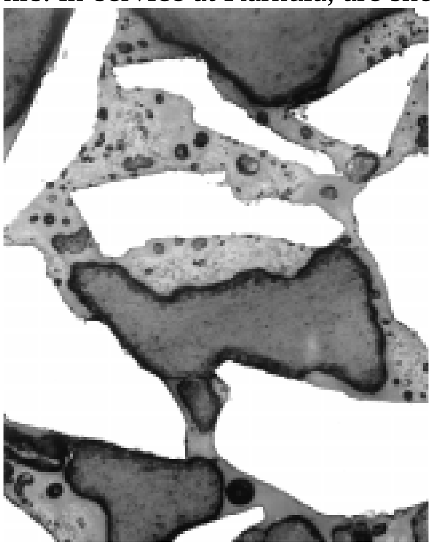

Figure 11. Photomicrograph of As-Manufactured Pall 326 Taken at 200X

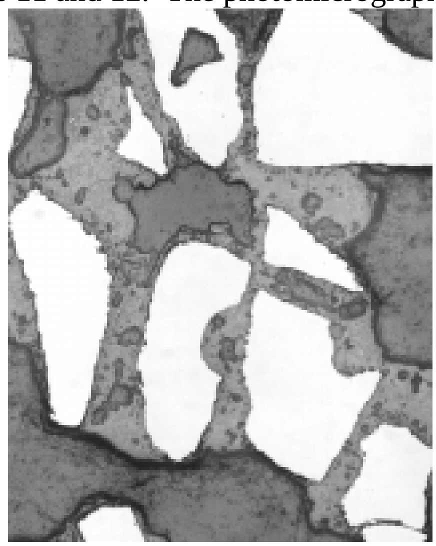

Figure 12. Photomicrograph of Pall 326 After 1166 Hrs. In-Service at Karhula Taken at 200X

indicate that clusters of SiC particles were fully or nearly fully coated by the binder and bridges connected these clusters. Numerous small pores and cracks are seen throughout the binder material although, as with Schumacher materials, the structure of this material does not readily propagate cracks. The pores in the 326 binder have curved boundaries with no sharp corners, typical of amorphous materials like glass. A cube of Pall 326 measuring 1/4 - 3/8 inch on each side was placed in hydrofluoric acid at 70 °F and within 2 hrs. the binder was removed. Small scattered white particles were observed in the residue after reaction with hydrofluoric acid and alumina was seen in EDS. The binder appears to be a non-translucent clay with alumina and some free glass (free silica). Photomicrographs of Pall 326 after 1166 hrs. at Karhula show evidence of chemical attack around the binder as well as increased cracking within the binder. Some pores in the binder after service at Karhula are open on the edges of the binder, evidence of chemical attack around the edges of the binder. As with the previously tested Pall 442T, the behavior of Pall 326 is controlled by the properties of the binder. Free silica in the 326 binder will lead to high temperature creep and susceptibility to chemical attack in the PFBC environment; however, property measurements and microstructural evaluations both indicate that Pall 326 showed improvements over Pall 442T.

Future testing of Pall 326 will focus on establishing operating limits. Tensile evaluations will be used to assess property degradation in the PFBC environment, creep tests on as-manufactured and used filters will be used to assess load and temperature levels where this material can operate without creep failure, microstructural examinations will be used to better define the chemical properties of the binder, and higher magnification photomicrographs will be used to examine the integrity of the particle/binder interface in both as-manufactured and used material.

Conclusions

Based on test results the following conclusions were obtained:

Schumacher FT20 and Pall 326 have lower room temperature tensile strengths than Schumacher F40 and Pall 442T but in the operating range of 1400 °F to 1600 °F the tensile strengths are near the same.

Property degradation in the PFBC environment is less severe for Schumacher FT20 and Pall 326 than for Schumacher F40 and Pall 442T. Schumacher FT20 lost less than 10% of its room temperature tensile strength after service at Karhula and Pall 326 lost from 15% to 30% of its tensile strength after service at Karhula.

Creep rates were about an order of magnitude lower for Schumacher FT20 and Pall 326 than for Schumacher F40 and Pall 442T and creep began to occur at 100 °F to 200 °F higher temperature; however, creep and stress rupture persisted.

Microscopic examination indicated that properties of the binder control the behavior of Schumacher FT20 and Pall 326 and that the binder in both materials contains free silica. Therefore, high temperature creep and property degradation due to chemical attack in the PFBC environment will occur in these materials.

Chemical attack around the edges of the binder was evident in Schumacher FT20 and Pall 326 in photomicrographs after 1166 hrs. in-service at Karhula.

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